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Investigation on the Equilibrium Phase Diagrams of the Ternary Systems $CdCl_2-RECl_3-H_2O$ (RE = La, Nd, Sm, Eu) at 303 K

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Equilibrium phase relations and the solubility data for the rare earth trichloride $RECl_3 \cdot nH_2O$ (RE = La, $n = 7$; RE = Nd, Sm, Eu, $n = 6$) and cadmium chloride $CdCl_2 \cdot 2.5H_2O$ in the aqueous system were investigated. The corresponding equilibrium phase diagrams in the ternary system $CdCl_2-RECl_3-H_2O$ at 303 K were constructed. The results showed that these systems were complicated and consisted of four stable equilibrium solid phases [$CdCl_2 \cdot H_2O$, $CdCl_2 \cdot 2.5H_2O$, $Cd_4RECl_{11} \cdot nH_2O$ ($n = 12$, 14, 4:1 type), $RECl_3 \cdot 7H_2O$] and a metastable phase [$Cd_8RECl_{19} \cdot 16H_2O$ (8:1 type)]. The new compounds $Cd_4RECl_{11} \cdot nH_2O$ and $Cd_8RECl_{19} \cdot 16H_2O$ were found to be incongruently soluble in the systems. The 4:1 type compounds obtained were identified and characterized by the method of X-ray diffraction, thermogravimetry, and differential thermogravimetry (TG, DTG).

Introduction

Equilibrium phase diagrams of the quaternary systems $CsCl-REX_3-HX-H_2O$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, and Y; X = Cl, Br) were investigated. The corresponding solubilities were determined in our previous studies.[1−7] It is highly valuable and important for us to understand the phase relations and interactions of CsCl and $RECl_3$ in the aqueous medium. We found new compounds in these systems such as the 4:1 type $Cs_4GdCl_7 \cdot H_2O$, 5:3 type $Cs_5Dy_3Br_{14} \cdot 24H_2O$, and 5:2 type $Cs_5RE_2Br_{11} \cdot 22H_2O$. Moreover, the research results on these systems showed that the rare earth trichlorides have both comparabilities and dissimilarities, thus confirming that lanthanide rare earth elements are bordered by the Gd element showing "the effect of two groups" before and after Gd in the aqueous phase equilibrium of the quaternary system.[6,7] These discoveries sparked us to further study phase equilibria systematically and find new types of compounds formed in the aqueous systems that had not been reported earlier in the related literature.

As a part of the systematic investigation on the ternary systems of rare earth chlorides (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Y), the phase diagrams of the $CdCl_2$-$RECl_3$-H_2O (RE = Ce, Pr, Dy, Y) ternary systems at 298 K have been determined in our previous reports.[8−11] Zhuo et al.[8] reported the presence of five equilibrium solid-phase regions ($CdCl_2 \cdot 2.5H_2O$, $CdCl_2 \cdot H_2O$, $Cd_4CeCl_{11} \cdot 12H_2O$, $Cd_6CeCl_{15} \cdot 14H_2O$, and $CeCl_3 \cdot 7H_2O$) in the $CdCl_2-CeCl_3-H_2O$ ternary system, of which the $Cd_4CeCl_{11} \cdot 12H_2O$ (4:1 type) was a stable and $Cd_6CeCl_{15} \cdot 14H_2O$ (6:1 type) was a metastable complex. For the $CdCl_2-PrCl_3-H_2O$ system,[9] four stable equilibrium solid phases ($CdCl_2 \cdot 2.5H_2O$, $CdCl_2 \cdot H_2O$, $Cd_4PrCl_{11} \cdot 12H_2O$, and $PrCl_3 \cdot 7H_2O$) and a metastable equilibrium phase ($Cd_8PrCl_{19} \cdot 20H_2O$) were observed. Qiao et al. re-examined the $CdCl_2-YCl_3-H_2O$[10] and $CdCl_2-DyCl_3-H_2O$[11] systems and confirmed the presence of two stable complexes ($Cd_4YCl_{11} \cdot 13H_2O$ and $Cd_5Y_2Cl_{16} \cdot 26H_2O$) and one metastable complex ($Cd_8YCl_{19} \cdot 15H_2O$) in the $CdCl_2-YCl_3-H_2O$ ternary system, not to mention the $YCl_3 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$ and $CdCl_2 \cdot H_2O$ phases. At the same time, they affirmed that the $CdCl_2-DyCl_3-H_2O$ system is composed of four stable equilibrium solid phases: $CdCl_2 \cdot 2.5H_2O$, $CdCl_2 \cdot H_2O$, $Cd_9Dy_2Cl_{21} \cdot 29H_2O$, and $DyCl_3 \cdot 6H_2O$, respectively. The present paper is on the phase chemical relations of cadmium

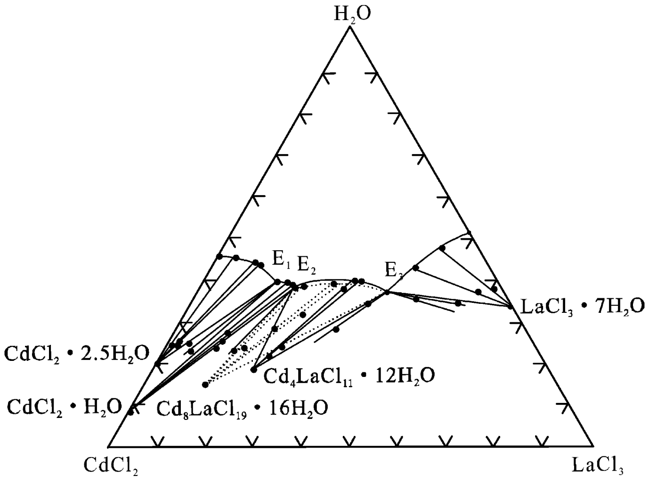

Figure 1. Isothermal solubility diagram of the system $CdCl_2-LaCl_3-H_2O$ at 303 K.

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Table 1. Solubility Data of the Ternary System $CdCl_2-LaCl_3-H_2O$ at 303 K

	composition of saturated solution (%)[a]		composition of wet residue (%)		
no.	$CdCl_2$	$LaCl_3$	$CdCl_2$	$LaCl_3$	solid phase[b]
1	54.65	0.00	80.28	0.00	A
2	52.24	3.33	74.00	0.40	A
3	48.64	7.92	72.13	2.05	A
4	47.22	9.20	72.91	2.21	A
5	46.88	10.74	71.97	2.41	A
6	45.41	15.40	70.31	4.63	A
7	45.71	15.02	70.90	5.97	A + A_1
8	44.40	17.67	60.99	11.04	A_1
9	44.39	17.87	67.19	9.36	A_1
10	43.64	18.87	63.26	11.65	A_1
11	43.58	19.44	64.69	10.51	A_1
12	42.54	19.61	61.92	14.84	A_1 + B
13	42.32	19.56	51.61	17.92	B
14	41.82	20.40	60.05	15.75	B
15	41.04	21.12	52.84	18.23	B
16	33.81	28.22	42.50	25.30	B
17	33.63	27.17	60.08	17.94	B
18	32.88	28.11	54.85	19.71	B
19	30.79	31.21	55.38	21.77	C
20	29.47	31.86	52.79	23.12	C
21	23.99	38.88	27.93	37.21	C
22	24.65	38.30	37.95	32.82	C + D
23	23.95	39.14	19.26	45.74	C + D
24	23.65	39.66	10.87	54.83	C + D
25	20.06	41.08	7.19	56.40	D
26	15.78	41.77	5.28	58.12	D
27	7.89	45.52	2.05	60.59	D
28	0.00	48.32	0.00	66.04	D

[a] Double saturation point (average). E_1: $CdCl_2$, 45.56 %; $LaCl_3$, 15.21 %. E_2: $CdCl_2$, 42.81 %; $LaCl_3$, 19.53 %. E_3: $CdCl_2$, 24.06 %; $LaCl_3$, 39.0 %. [b] Complexes: A, $CdCl_2{\cdot}2.5H_2O$; A_1, $CdCl_2{\cdot}H_2O$; B, $Cd_8LaCl_{19}{\cdot}16H_2O$; C, $Cd_4LaCl_{11}{\cdot}12H_2O$; D, $LaCl_3{\cdot}7H_2O$.

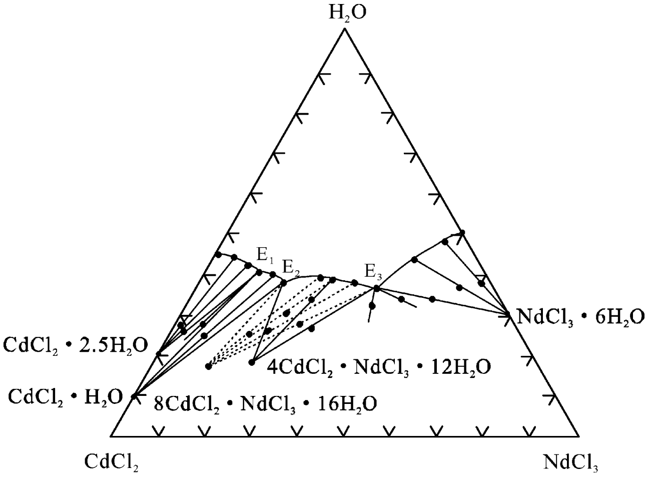

Figure 2. Isothermal solubility diagram of the system $CdCl_2-NdCl_3-H_2O$ at 303 K.

chloride and light rare earth trichlorides in the $CdCl_2-RECl_3-H_2O$ (RE = La, Nd, Sm, Eu) systems. The aim is try to find more phase equilibria information on the $CdCl_2-RECl_3-H_2O$ ternary systems.

Experimental Section

Preparing Samples. $CdCl_2{\cdot}2.5H_2O$, RE_2O_3 (RE = La, Nd, Sm, Eu), and 37 mass % HCl are of AR grade (all commercially available). $RECl_3{\cdot}nH_2O$ (n = 6 or 7) was crystallized from the solution of RE_2O_3, which was reacted with hydrochloric acid (37 mass % HCl). For detailed information on the preparation of $RECl_3{\cdot}6H_2O$ or $RECl_3{\cdot}7H_2O$, see ref 12. The compositions of $RECl_3{\cdot}nH_2O$ were determined by analyzing Cl^- content by titration with a normal solution of silver nitrate (0.1318 $mol{\cdot}dm^{-3}$) and RE^{3+} content by titration with EDTA solution (0.02247 $mol{\cdot}dm^{-3}$). The purity of the chemicals reached this way was found to be about 99.9 mass %. The analysis errors for those ions were relative and found to be better than ± 0.2 %.

Table 2. Solubility Data of the Ternary System $CdCl_2-NdCl_3-H_2O$ at 303 K

	composition of solution (%)[a]		composition of wet residue (%)		
no.	$CdCl_2$	$NdCl_3$	$CdCl_2$	$NdCl_3$	solid phase[b]
1	54.65	0.00	80.28	0.00	A
2	51.23	4.70	71.84	0.55	A
3	49.71	7.66	71.32	1.59	A
4	49.71	8.38	71.48	2.37	A
5	47.68	8.62	70.97	2.14	A
6	48.54	10.17	64.35	5.53	A
7	47.96	11.80	66.30	5.94	A + A_1
8	47.68	11.09	66.58	6.27	A_1
9	45.19	14.95	67.53	7.56	A_1
10	45.44	15.26	65.54	7.94	A_1
11	45.4	15.06	61.13	9.79	A_1
12	44.53	15.60	59.03	11.09	A_1
13	44.94	15.81	63.92	9.09	A_1
14	44.29	17.97	65.14	10.31	A_1
15	44.10	18.01	59.54	14.17	A_1 + B
16	43.45	19.13	52.37	17.22	B
17	35.74	24.92	57.86	17.05	B
18	32.63	28.57	46.71	22.58	B
19	44.05	18.19	52.58	18.22	C
20	32.96	28.04	39.85	26.52	C
21	29.33	32.93	45.88	26.71	C
22	30.31	32.45	45.50	27.26	C
23	27.87	35.02	39.27	29.96	B
24	25.13	37.59	43.13	30.07	C
25	24.63	37.51	32.15	36.47	C + D
26	25.17	39.19	27.98	39.70	C + D
27	24.87	37.82	21.07	45.15	C + D
28	24.76	38.57	14.88	51.77	D
30	21.51	39.49	12.83	51.28	D
31	21.42	39.76	8.80	56.73	D
32	13.24	43.74	6.99	56.41	D
34	4.43	47.52	2.09	59.52	D
35	0.00	49.52	0.00	70.03	D
36		50.23		69.03	D

[a] Double saturation point (average). E_1: $CdCl_2$, 47.82 %; $NdCl_3$, 11.45 %. E_2: $CdCl_2$, 44.15 %; $NdCl_3$, 18.06 %. E_3: $CdCl_2$, 24.91 %; $NdCl_3$, 38.14 %. [b] Complexes: A, $CdCl_2{\cdot}2.5H_2O$; A_1, $CdCl_2{\cdot}H_2O$; B, $Cd_8NdCl_{19}{\cdot}16H_2O$; C, $Cd_4NdCl_{11}{\cdot}12H_2O$; D, $NdCl_3{\cdot}6H_2O$.

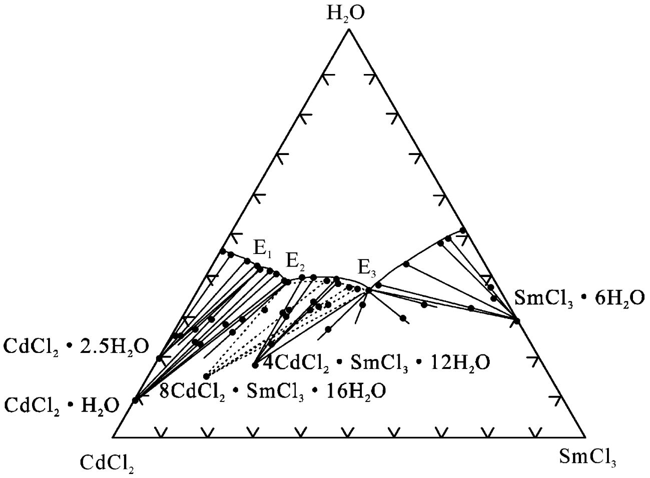

Figure 3. Isothermal solubility diagram of the system $CdCl_2-SmCl_3-H_2O$ at 303 K.

Investigations on the Ternary Systems at 303 K and Analysis Methods. The starting materials $CdCl_2{\cdot}2.5H_2O$, $RECl_3{\cdot}nH_2O$, and H_2O were mixed in different weight ratios. There were 28

Table 3. Solubility Data of the Ternary System $CdCl_2-SmCl_3-H_2O$ at 303 K

	composition of saturated solution (%)[a]		composition of wet residue (%)		
no.	$CdCl_2$	$SmCl_3$	$CdCl_2$	$SmCl_3$	solid phase[b]
1	54.05	0.00	80.28	0.00	A
2	52.16	2.97	74.25	0.20	A
3	49.73	7.08	72.81	2.04	A
4	49.33	7.41	71.29	1.26	A
5	48.76	9.55	72.99	1.91	A
6	48.26	9.57	70.81	1.69	A
7	47.77	11.07	69.32	4.24	A_1
8	46.86	13.32	70.31	5.87	A_1
9	45.91	13.68	77.11	3.35	A_1
10	44.89	15.14	70.31	6.33	A_1
11	44.32	17.70	61.38	10.70	A_1
12	43.58	18.41	57.64	13.35	A_1
13	43.35	18.41	78.40	4.51	A_1
14	43.22	18.32	61.06	13.26	$A_1 + B$
15	43.67	18.55	51.35	16.63	B
16	34.56	26.71	47.89	22.04	B
17	32.79	27.97	51.85	20.79	B
18	31.21	31.89	40.28	27.80	B
19	30.28	33.38	37.88	29.42	B
20	27.43	35.30	54.65	22.44	B
21	39.95	21.38	48.55	20.79	C
22	37.03	23.96	46.36	22.15	C
23	32.81	28.99	41.72	26.18	C
24	32.54	28.69	40.38	26.05	C
25	31.52	30.80	42.13	26.45	C
26	27.59	36.31	16.93	50.36	C + D
27	27.44	36.23	23.67	46.78	C + D
28	27.06	36.02	40.59	31.78	C + D
29	26.82	36.99	40.50	32.71	D
30	25.43	37.47	7.79	60.35	D
31	16.30	41.08	4.43	62.24	D
32	6.75	45.55	1.99	63.62	D
33	4.68	46.35	1.65	61.74	D
34	0.00	48.78	0.00	70.39	D

[a] Double saturation point (average). E_1: $CdCl_2$, 47.70 %; $SmCl_3$, 11.08 %. E_2: $CdCl_2$, 43.49 %; $SmCl_3$, 18.43 %. E_3: $CdCl_2$, 27.27 %; $SmCl_3$, 36.17%. [b] Complexes: A, $CdCl_2 \cdot 2.5H_2O$; A_1, $CdCl_2 \cdot H_2O$; B, $Cd_8SmCl_{19} \cdot 16H_2O$; C, $Cd_4SmCl_{11} \cdot 12H_2O$; D, $SmCl_3 \cdot 6H_2O$.

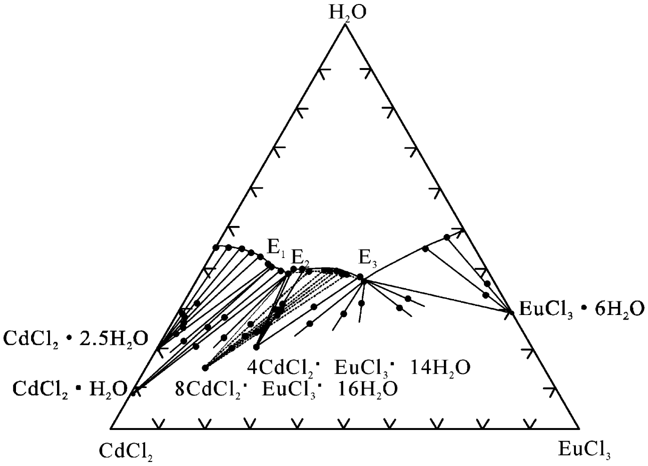

Figure 4. Isothermal solubility diagram of the system $CdCl_2-EuCl_3-H_2O$ at 303 K.

to 41 samples prepared. Each contained solid and liquid phases that were sealed in a plastic container. All the sealed samples were put in a big water tank with a thermostat fixed at 303 K and an electrical stirrer. The precision of the temperature was ± 1 K. The solid−liquid phase equilibrium was established for these samples after (6 to 10) days.

Table 4. Solubility Data of the Ternary System $CdCl_2-EuCl_3-H_2O$ at 303 K

	composition of saturated solution (%)[a]		composition of wet residue (%)		
no.	$CdCl_2$	$EuCl_3$	$CdCl_2$	$EuCl_3$	solid phase b
1	54.65	0.00	80.28	0.00	A
2	54.13	1.18	67.94	0.78	A
3	52.61	2.65	70.70	0.85	A
4	51.27	3.64	68.76	1.74	A
5	50.11	5.39	66.06	2.60	A
6	49.75	6.39	76.18	0.80	A
7	49.19	7.42	71.49	1.63	A
8	47.13	10.12	72.37	2.74	A
9	46.77	13.38	74.59	1.68	A
10	45.86	13.30	78.05	3.04	$A + A_1$
11	45.29	14.58	74.10	4.28	$A + A_1$
12	46.00	13.89	66.74	8.30	A_1
13	43.31	16.12	59.27	10.38	A_1
14	43.87	16.37	59.43	11.15	A_1
15	44.15	16.48	61.84	10.10	A_1
16	41.68	18.47	64.83	10.26	A_1
17	43.26	18.61	71.95	7.65	A_1
18	43.01	18.57	64.55	12.68	B
19	42.09	19.44	57.03	16.25	B
20	42.19	19.37	58.67	15.56	B
21	38.09	22.73	65.32	13.41	B
22	33.86	26.12	60.39	16.18	B
23	33.58	26.94	48.74	21.32	B
24	32.55	28.52	64.66	14.93	B
25	31.33	29.35	50.01	21.35	B
26	30.53	31.23	55.67	18.97	B
27	28.86	34.01	42.18	26.72	B
28	28.75	34.32	55.59	20.06	B
29	28.57	34.16	33.89	38.84	B + D
30	41.41	19.18	49.62	20.40	C
31	38.72	21.55	47.70	20.92	C
32	29.28	33.76	41.43	28.16	C
33	27.20	36.03	45.06	29.23	C + D
34	27.45	36.17	36.07	34.96	C + D
35	27.24	36.04	20.67	47.08	C + D
36	27.12	35.62	23.17	46.19	C + D
37	27.56	33.93	31.29	37.51	C + D
38	24.57	37.73	9.78	57.37	D
39	9.99	45.35	3.05	63.13	D
40	4.16	47.18	1.34	62.28	D
41	0.00	50.04	0.00	70.52	D

[a] Double saturation point (average). E_1: $CdCl_2$, 45.98 %; $EuCl_3$, 13.79 %. E_2: $CdCl_2$, 42.56 %; $EuCl_3$, 18.79%. E_3: $CdCl_2$, 27.30 %; $EuCl_3$, 36.08 %. [b] Complexes: A, $CdCl_2 \cdot 2.5H_2O$; A_1, $CdCl_2 \cdot H_2O$; B, $Cd_8EuCl_{19} \cdot 16H_2O$; C, $Cd_4EuCl_{11} \cdot 14H_2O$; D, $EuCl_3 \cdot 6H_2O$.

Table 5. X-ray Powder Diffraction Data of Compounds $Cd_4RECl_{11} \cdot nH_2O$ (RE = La, Nd, Sm, Eu)

	parameter							
compound	d/nm	I/I_0	d/nm	I/I_0	d/nm	I/I_0	d/nm	I/I_0
$Cd_4LaCl_{11} \cdot 12H_2O$	1.088	59	0.9646	100	0.5817	94	0.4892	18
	0.3276	22	0.2843	17	0.2609	12	0.1592	13
$Cd_4NdCl_{11} \cdot 12H_2O$	1.3580	24	0.8308	97	0.6197	99	0.5133	48
	0.4782	36	0.3324	36	0.2915	84	0.2741	34
$Cd_4SmCl_{11} \cdot 12H_2O$	1.3630	11	0.8308	93	0.6189	99	0.5847	14
	0.4156	35	0.3422	19	0.2914	22	0.2740	15
$Cd_4EuCl_{11} \cdot 14H_2O$	1.1660	38	0.8631	59	0.6954	99	0.5548	27
	0.4329	18	0.3904	53	0.2930	86	0.1733	20

Table 6. X-ray Powder Diffraction Data of Initial Compounds

	parameter							
compound	d/nm	I/I_0	d/nm	I/I_0	d/nm	I/I_0	d/nm	I/I_0
$CdCl_2 \cdot 2.5H_2O$	0.5850	100	0.2648	90	0.3270	70	0.1826	55
$LaCl_3 \cdot 7H_2O$	0.2630	100	0.2210	100	0.2360	80	0.6600	70
$NdCl_3 \cdot 6H_2O$	0.6500	100	0.3430	80	0.6006	30		
$SmCl_3 \cdot 6H_2O$	0.5950	100	0.5079	70	0.3569	50		
$EuCl_3 \cdot 6H_2O$	0.2500	100	0.2060	80	0.1468	40	0.211	30

The saturated solutions and the corresponding wet solid phases (wet residues) of the samples were separated, taken out, and analyzed. For the analysis methods, see ref 9. The composition of the new compounds in the systems was determined by the well-known wet residue method of Schreinemakers[13] and checked by chemical analysis. The results of

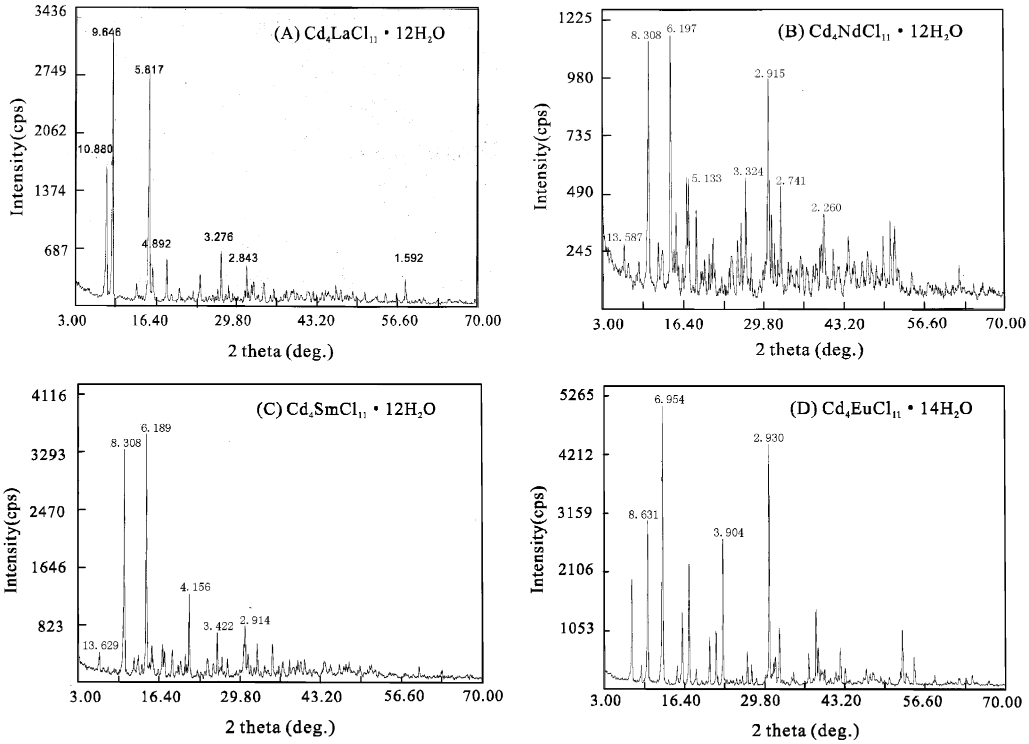

Figure 5. X-ray powder diffraction spectrum of (A) $Cd_4LaCl_{11}·12H_2O$, (B) $Cd_4NdCl_{11}·12H_2O$, (C) $Cd_4SmCl_{11}·12H_2O$, and (D) $Cd_4EuCl_{11}·14H_2O$ compounds.

analyses for the ternary systems are shown in Tables 1 to 4, respectively.

Equipment and Conditions. Thermal characterization of the new compounds was undertaken with a Parkin-Elmer TGA7/4(TG−DTG) thermoanalyzer that worked with a heating rate of 10 K/min under an Ar atmosphere with a flow rate of 60 $cm^3·min^{-1}$. X-ray diffraction (XRD) measurements were performed in air by a D/Max-3C diffractometer using CuKα radiation, 50kV, and 80 mA at room temperature.

Results and Discussion

$CdCl_2 + RECl_3 + H_2O$ (RE = La, Nd, Sm, Eu) Systems at 303 K. The solubility data of the $CdCl_2-RECl_3-H_2O$ (RE = La, Nd, Sm, Eu) ternary systems at 303 K are listed in Tables 1 to 4, respectively. Figures 1 to 4 depict the corresponding phase equilibrium diagrams, respectively.

As can be seen in Figure 1, the curves of solubility consist of five branches in the ternary system $CdCl_2-LaCl_3-H_2O$, which correspond to the equilibrium solid phases $CdCl_2·2.5H_2O$ (A), $CdCl_2·H_2O$ (A_1), $Cd_8LaCl_{19}·16H_2O$ (B), $Cd_4LaCl_{11}·12H_2O$ (C), and $LaCl_3·7H_2O$ (D), respectively. This indicates that the phase regions of three new compounds $CdCl_2·H_2O$ (A_1), $Cd_8LaCl_{19}·16H_2O$ (B), and $Cd_4LaCl_{11}·12H_2O$ (C) are formed in this system except for initial compounds A and D, of which compound B (8:1 type) is a metastable (dashed line) one while the C (4:1 type) is a stable one. Both of them are incongruently soluble in the aqueous system. The presence of the $CdCl_2·H_2O$ (A_1) in the $CdCl_2-LaCl_3-H_2O$ system implies that $LaCl_3$ can dehydrate crystal water from the $CdCl_2·2.5H_2O$. The compounds of 8:1 type and 4:1 type have not been synthesized and reported in literature so far.

As far as the ternary system $CdCl_2-LaCl_3-H_2O$ is concerned, the equilibrium of the solid-phase regions was established after 5 days, and the metastable $Cd_8LaCl_{19}·16H_2O$ (8:1 type) detected by Schreinemakers method was relatively more precipitated in the first (5 to 6) days while the stable $Cd_4LaCl_{11}·12H_2O$ (4:1 type) was relatively less precipitated. The amount of stable $Cd_4LaCl_{11}·12H_2O$ was found to increase gradually after 8 days. This indicates that the $Cd_8LaCl_{19}·16H_2O$ complex in the aqueous system easy changed into $Cd_4LaCl_{11}·12H_2O$ with increasing equilibrium time. This is just the cause of the mutual superposition of both phase regions $Cd_8LaCl_{19}·16H_2O$ and $Cd_4LaCl_{11}·12H_2O$ (see Figure 1) and an explanation why the 8:1 type was a metastable complex. Therefore, the 8:1 type complex is difficult to obtain from the ternary system $CdCl_2-LaCl_3-H_2O$, while the 4:1 type is obtained easily. The results of chemical analyses for the 4:1 type compound in mass percent are 20.79 % $LaCl_3$ and 61.06 % $CdCl_2$ (theoretical: 20.53 % $LaCl_3$, 61.39 % $CdCl_2$). This indicates that the compositions of the solid compounds determined by the Schreinemakers method are reliable.

We noticed in previous studies that the complexes of the 8:1 type and 4:1 type existed in the quaternary systems $CdCl_2-LaCl_3-HCl-H_2O$[14] and $CdCl_2-PrCl_3-HCl-H_2O$.[9] They were congruently soluble and stable compounds. More importantly, both complexes were easy prepared from the quaternary system, a feature that differs from the ternary systems. This is probably caused by the existence of hydrochloric acid in the quaternary system. Moreover, the similar effects were observed in the $CdCl_2-CeCl_3-H_2O$ as well as $CdCl_2-CeCl_3-HCl-H_2O$ systems.[8] This indicated that the phase behaviors for the light rare earth elements La, Ce, and Pr in the $CdCl_2-RECl_3-HCl-H_2O$ quaternary systems or $CdCl_2-RECl_3-H_2O$ ternary systems are similar.

Comparison between the Ternary Systems. As may be seen from Figures 2 to 4, the $CdCl_2-RECl_3-H_2O$ (RE = Nd, Sm, Eu) systems belong to the same category as the $CdCl_2-LaCl_3-H_2O$ system. Five solubility curves correspond respectively to the compounds of $CdCl_2·2.5H_2O$ (A), $CdCl_2·H_2O$ (A_1), $Cd_8RECl_{19}·16H_2O$ (B), $Cd_4RECl_{11}·nH_2O$ (C, RE = Nd, Sm, n = 12; RE = Eu, n = 14), and $RECl_3·6H_2O$ (RE = Nd, Sm, Eu). The new compounds $Cd_8RECl_{19}·16H_2O$ of 8:1 type (B) formed in these aqueous systems are metastable (dashed line) complexes while the $Cd_4RECl_{11}·nH_2O$ of 4:1 type (C) complexes are the

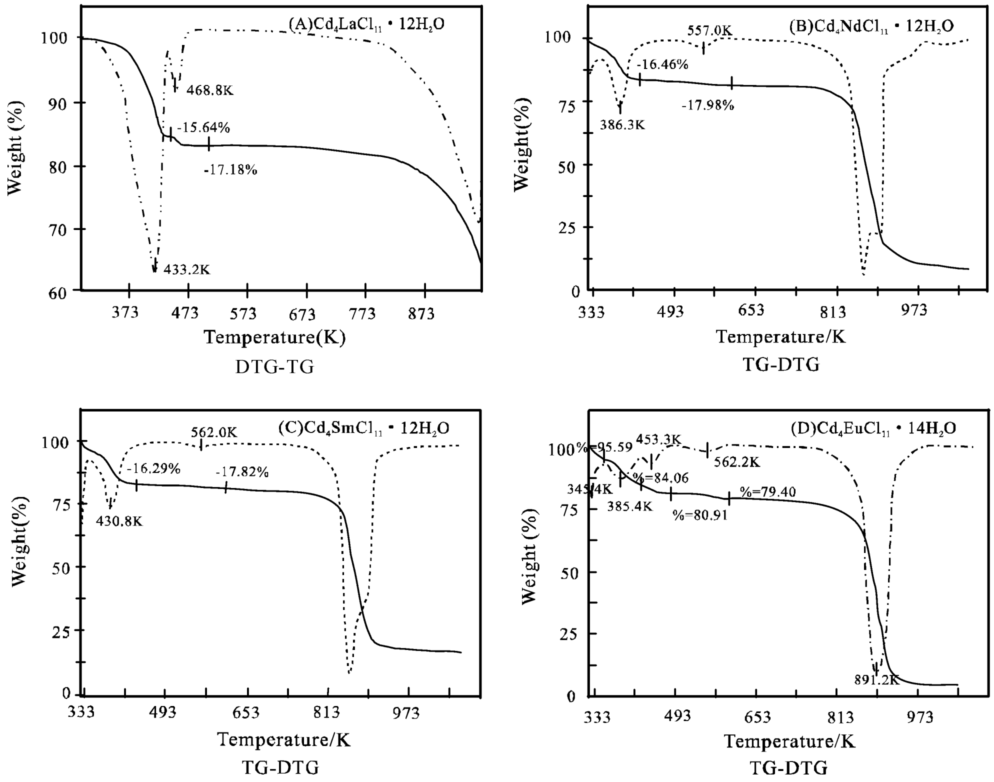

Figure 6. Thermogravimetric curves of the (A) $Cd_4LaCl_{11}\cdot 12H_2O$, (B) $Cd_4NdCl_{11}\cdot 12H_2O$, (C) $Cd_4SmCl_{11}\cdot 12H_2O$, and (D) $Cd_4EuCl_{11}\cdot 14H_2O$ compounds. —, TG; - - -, DTG.

Table 7. TG−DTG Data of Compounds $Cd_4RECl_{11}\cdot nH_2O$ (RE = La, Nd, Sm, Eu)

compound	lost water number	peak temp/K	loss of wt/%		product
		DTG	experimental	theoretical	
$Cd_4LaCl_{11}\cdot 12H_2O$	lost $11H_2O$	433.2	16.06	16.57	$Cd_4LaCl_{11}\cdot H_2O$
	lost H_2O	468.8	1.54	1.51	Cd_4LaCl_{11}
	lost $12H_2O$		17.60	18.08	
$Cd_4NdCl_{11}\cdot 12H_2O$	lost $11H_2O$	386.3	16.46	16.50	$Cd_4NdCl_{11}\cdot H_2O$
	lost $1H_2O$	557.0	1.52	1.50	Cd_4NdCl_{11}
	lost total $12H_2O$		17.98	18.00	
$Cd_4SmCl_{11}\cdot 12H_2O$	lost $11H_2O$	430.8	16.29	16.42	$Cd_4SmCl_{11}\cdot H_2O$
	lost $1H_2O$	562.0	1.53	1.49	Cd_4SmCl_{11}
	lost total $12H_2O$		17.82	17.91	
$Cd_4EuCl_{11}\cdot 14H_2O$	lost $3H_2O$	345.4	4.41	4.35	$Cd_4EuCl_{11}\cdot 11H_2O$
	Lost $8H_2O$	385.4	11.53	11.6	$Cd_4EuCl_{11}\cdot 3H_2O$
	Lost $2H_2O$	453.3	3.15	2.90	$Cd_4EuCl_{11}\cdot H_2O$
	Lost $1H_2O$	562.2	1.51	1.45	Cd_4EuCl_{11}
	lost total $14H_2O$		20.25	20.26	

stable ones. As stated above, both the 8:1 type and the 4:1 type compounds were incongruently soluble in the aqueous systems. The results of the chemical analyses for the 4:1 type complexes (in mass percent) are 20.64 % $NdCl_3$ and 60.88 % $CdCl_2$ for the $Cd_4NdCl_{11}\cdot 12H_2O$; 20.86 % $SmCl_3$ and 61.24 % $CdCl_2$ for the $Cd_4SmCl_{11}\cdot 12H_2O$; and 20.46 % $EuCl_3$ and 58.33 % $CdCl_2$ for the $Cd_4EuCl_{11}\cdot 14H_2O$, which agree well with the theoretical values 20.89 % $NdCl_3$, 61.11 % $CdCl_2$, and 21.29 % $SmCl_3$ and 60.80 % $CdCl_2$, 20.78% $EuCl_3$, and 58.96% $CdCl_2$, respectively.

Characterization of the New Complexes Obtained from the Four Systems. Two kinds of the eight new complexes were found in the present ternary systems, which have not been reported in literature. Only X-ray powder diffraction data of the four compounds $Cd_4RECl_{11}\cdot nH_2O$ (RE = La, Nd, Sm, and Eu) of the 4:1 type are given in Table 5 due to the difficulty of obtaining similar data for the 8:1 type compounds directly. They are obviously quite different from the X-ray diffraction data of the initial compounds $CdCl_2\cdot 2.5H_2O$ and $RECl_3\cdot nH_2O$[15] (see Table 6). Figure 5 (panels A to D) contains the X-ray powder diffraction patterns of the $Cd_4RECl_{11}\cdot nH_2O$ (RE = La, Nd, Sm, and Eu) compounds. These data and patterns indicate that the four compounds are new substances.

Thermogravimetry and differential thermogravimetry (TG, DTG) data of the $Cd_4RECl_{11}\cdot nH_2O$ (RE = La, Nd, Sm, and Eu) compounds in comparison with the theoretical weight losses are listed in Table 7; the corresponding graphs are displayed in Figure 6 (panels A to D). The purpose of the thermal analysis was to confirm the contents of crystal water in the $Cd_4RECl_{11}\cdot nH_2O$ compounds and to investigate the dehydrating properties of the 4:1 type complexes. Based on the total mass-loss values of the various complexes and their peak temperatures of dehydrating steps in the different range of temperatures, we suggest the dehydration equations for the four complexes:

$$Cd_4LaCl_{11}\cdot 12H_2O \xrightarrow[433\ K]{-11H_2O} Cd_4LaCl_{11}\cdot H_2O \xrightarrow[469\ K]{-H_2O} Cd_4LaCl_{11} \quad (1)$$

$$Cd_4NdCl_{11}\cdot 12H_2O \xrightarrow[386\ K]{-11H_2O} Cd_4NdCl_{11}\cdot H_2O \xrightarrow[557\ K]{-H_2O} Cd_4NdCl_{11} \tag{2}$$

$$Cd_4SmCl_{11}\cdot 12H_2O \xrightarrow[431\ K]{-11H_2O} Cd_4SmCl_{11}\cdot H_2O \xrightarrow[562\ K]{-H_2O} Cd_4SmCl_{11} \tag{3}$$

$$Cd_4EuCl_{11}\cdot 14H_2O \xrightarrow[345\ K]{-3H_2O} Cd_4EuCl_{11}\cdot 11H_2O \xrightarrow[385\ K]{-8H_2O} Cd_4EuCl_{11}\cdot 3H_2O \xrightarrow[453\ K]{-2H_2O} Cd_4EuCl_{11}\cdot H_2O \xrightarrow[562\ K]{-H_2O} Cd_4EuCl_{11} \tag{4}$$

Conclusions

The solubilities of the ternary systems $CdCl_2-RECl_3-H_2O$ (RE = La, Nd, Sm, and Eu) at 303 K were measured, and the corresponding phase diagrams were constructed. The compositions of the solid phases were determined by the Schreinemakers method and confirmed by chemical analysis. Two kinds of the new compounds ($CdCl_2$:$RECl_3$) of 8:1 type and 4:1 type were found to exist in the above systems besides the earlier reported systems $CdCl_2-CeCl_3-H_2O$ and $CdCl_2-PrCl_3-H_2O$. The 8:1 type compounds are unstable for the complexes, while the 4:1 type compounds are stable. Both of them are incongruently soluble in the ternary systems. These results showed that the phase equilibrium regions and the composition of the new compounds (the 8:1 or 4:1 type) in the ternary systems $CdCl_2-RECl_3-H_2O$ (RE = La, Ce, Pr, Nd, Sm, and Eu) are very similar. It should be noted that these rare earth elements are all in front of Gd in the lanthanide series. This indicates the similarity of light rare earth elements in the phase equilibria behaviorus. Comparing the reported quaternary systems containing also HCl with the present ternary systems, the discussion in the preceding sections has shown that the compounds of the 8:1 type and the 4:1 type were present in both kinds of systems, but the compounds of the 8:1 and the 4:1 types are congruently soluble in the quaternary system and incongruently soluble in the ternary system.

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